$CH_2CH_2CH_2$); $^{13}C$ NMR (62.89 MHz, $CDCl_3$) $\delta$ 146.5, 139.1, 115.7, 113.2, 84.7, 68.3, 31.4, 28.9, 28.5, 27.8, 18.6; mass spectrum, *m/e* (100 eV, CI, isobutane, rel intens) 149 ($MH^+$, 47), 119 (53), 107 (82), 105 (45), 95 (65).

**9-Methylene-10-undecen-2-ynoic Acid, Methyl Ester (8).** To a THF solution (75 mL) of 3-methylene-1-decen-9-yne (1.90 g, 12.8 mmol) at -78 °C was added dropwise *n*-BuLi (13.0 mmol). The reaction was stirred for 5 min at -78 °C before addition of methyl chloroformate (1.0 mL, 13 mmol). After being stirred for 1 h at -78 °C, the reaction was permitted to warm to 0 °C and then quenched by pouring into $H_2O$ (100 mL) and extracting the aqueous layer with petroleum ether (3 × 100 mL). Purification by flash column chromatography on silica gel gives 2.35 g (89%) of dienyne ester (**8**): IR ($CCl_4$) 3095, 2945, 2865, 2240, 1725, 1595, 1435, 1210, 1075, 900, 890 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 6.37 (dd, $J$ = 17.6, 10.8 Hz, 1 H, $CH$=$CH_2$), 5.23 (d, $J$ = 17.6 Hz, 1 H, CH=$CH_2$), 5.06 (d, $J$ = 10.8 Hz, 1 H, CH=$CH_2$), 4.99 (s, 1 H, C=$CH_2$), 3.77 (s, 3 H, $CO_2CH_3$), 2.35 (t, $J$ = 7.0 Hz, 2 H, -$CH_2$C≡C), 2.22 (br t, $J$ = 7 Hz, 2 H, =C$CH_2CH_2$); $^{13}C$ NMR (62.89 MHz, $CDCl_3$) $\delta$ 154.4, 146.4, 139.1, 115.8, 113.3, 89.9, 73.1, 52.7, 31.3, 28.9, 27.7, 27.6, 18.8; mass spectrum, *m/e* (100 eV, CI, isobutane, rel intens) 207 ($MH^+$, 52), 175 (13), 147 (100); high-resolution mass spectrum, *m/e* (70 eV, EI) calcd $C_{13}H_{18}O_2$ 206.1307, obsd 206.1324.

**3-Methylene-1-undecene (17).** Octyl iodide (2.84 g, 11.8 mmol) and a THF solution (1.4 mL) of $Li_2CuCl_4$ (0.3 M) were treated dropwise over 20 min with a chloroprene Grignard solution (14.2 mL, 14.2 mmol) (exotherm). After the addition, the solution was treated with saturated $NH_4Cl$ (100 mL) and extracted with pentane. Purification was accomplished by flash chromatography; the product was isolated in 75-80% yield. For kinetic runs, small amounts of material were purified by preparative GC. Diene **17**: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 6.37 (dd, $J$ = 17.5, 10.8 Hz, 1 H), 5.25 (dd, $J$ = 17.5, 0.71 Hz, 1 H), 5.05 (dd, $J$ = 10.8, 0.79 Hz, 1 H), 4.9 (m, 2 H), 2.22 (t, $J$ = 7.14 Hz, 2 H), 1.5 (m, 2 H), 1.3 (m, 10 H), 0.9 (t, $J$ = 6.38 Hz, 3 H); $^{13}C$ NMR (62.86 MHz, $CDCl_3$) $\delta$ 146.93, 139.30, 115.66, 113.26, 32.15, 31.63, 29.89, 29.75, 29.55, 28.44, 22.90, 14.36; IR (NaCl, neat) 3450, 3110, 2920, 2870, 1600, 1470, 990, 900 $cm^{-1}$; mass spectrum, *m/e* (100 eV, isobutane, rel intens) 167 (66), 153 (14), 139 (17); mass spectrum, *m/e* (EI, direct inlet) 166 (1), 155 (7).

Cycloadducts **19** and **20**: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 5.4 (s, 1 H), 4.35 (s, 2 H), 3.7-3.8 (3 H), 3.3 (3 H), 2.8-3.0 (3 H), 2.0 (t, 2 H), 1.2-1.4 (13 H), 0.8-0.9 (t, 3 H); $^{13}C$ NMR (62.86 MHz, $CDCl_3$) $\delta$ 168.4, 144.1 (144.0), 134.6 (134.1), 117.0 (116.7), 72.8 (72.6), 59.5 (58.8), 58.4 (58.2), 52.9 (51.9), 51.5 (51.3), 36.9 (36.2), 32.0 (31.9), 31.1 (29.8), 29.6 (29.6), 29.4 (29.4), 29.3 (28.9), 27.5 (27.4), 22.8, 14.2; IR (neat) 2942, 2875, 1730, 1440, 1260, 1220, 1125, 737 $cm^{-1}$; mass spectrum, *m/e* (70 eV, CI, isobutane, rel intens) 295 (100), 293 (86), 263 (43), 261 (48); high-resolution mass spectrum, *m/e* (70 eV, EI) calcd ($M^+$) 294.2194, obsd 294.2151.

Cycloadduct **21**: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 5.4-5.5 (s, 1 H), 3.74 (s, 3 H), 2.9-3.0 (2 H), 2.6-2.75 (2 H), 2.05 (s, 3 H), 1.9-2.0 (2 H), 1.2-1.4 (12 H), 0.8-0.9 (3 H); $^{13}C$ NMR (62.86 MHz, $CDCl_4$) $\delta$ 168.9, 144.2, 133.6, 121.7, 118.0, 51.3, 38.1, 36.7, 32.1, 29.7, 29.6, 29.5, 28.9, 27.4, 22.9, 21.5, 14.3; IR (neat) 2950, 2879, 1720, 1650, 1440, 1250, 1070, 910, 735 $cm^{-1}$; mass spectrum, *m/e* (70 eV, rel intens) 265 (100), 263 (18), 151 (3); high-resolution mass spectrum, *m/e* (70 eV, EI) calcd 264.2088, obsd 264.2068.

Cycloadduct **23** and **24**: $^1H$ NMR ($CDCl_3$, 250 Mz) $\delta$ 5.65 (s, 1 H), 4.58 (s, 2 H), 4.5 (s, 2 H), 3.9-4.05 (6 H), 3.76 (t, 2 H), 3.55 (3 H), 3.0-3.3 (3 H), 2.25 (t, 2 H), 1.8 (4 H), 1.1 (1 H); $^{13}C$ NMR ($CDCl_3$, 62.86 MHz) $\delta$ 168.4, 153.7, 144.11 (143.81), 134.22 (133.72), 124.25 (124.14), 117.66 (117.32), 84.25, 72.82 (72.74), 70.96 (70.77), 58.48 (58.03), 52.86 (51.54), 36.56, 31.98 (31.18), 29.89, 29.30, 28.99; IR ($CDCl_4$, solution cell) 2960, 2884, 2250, 1735, 1725, 1647, 1440, 1260 (B), 1220, 1120, 1063 $cm^{-1}$; mass spectrum, *m/e* (CI, direct inlet) 351 (5.91), 350 (0.23), 319 (100); mass spectrum, *m/e* (EI, direct inlet) 350 (4.09); high-resolution mass spectra, calcd 350.1718, obsd 350.1735.

**Kinetic Studies.** Rate constants for the intramolecular Diels-Alder cycloaddition of dienyne esters **4**, **6**, and **8** were obtained as follows. Microthermolysis solutions (125 $\mu$L) were prepared from a benzene solution (10.0 mL) of dienyne ester (10 mg) and cyclododecane (internal standard). The solutions were thermolyzed at the specified temperatures in a molten salt bath with temperature control to within ±0.2 °C. The individual tubes were removed, rapidly quenched by cooling, and then analyzed by capillary GC. First-order kinetics were observed from which the calculated rate constants are as follows: temperature (°C), $k \times 10^6$ ($s^{-1}$).

Dienyne **8**: 210, 4.6; 220, 7.2; 246, 29; 258, 59.

Dienyne **6**: 226.8, 2.14; 234.4, 2.90; 245.0, 5.71; 249.9, 7.06; 258.0, 9.90.

Dienyne **4**: 170.4, 0.33; 185.2, 0.745; 195.1, 1.27; 200.2, 1.81; 208.5, 2.75; 210.0, 2.83.

Dienyne **12**: 193.3, 2.36; 209.5, 5.00; 223.5, 10.6; 236.8, 17.7.

Rate constants for the bimolecular reactions and competitions between **12** and **16** were extracted by fitting the observed time-concentration profiles with simulated profiles using adjustable rate constants. Rate constants were adjusted to minimize the root-mean-square deviation between the observed and calculated time-concentration values.

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**Registry No. 4**, 86532-33-4; **5**, 86532-36-7; **6**, 111772-51-1; **7**, 111772-52-2; **8**, 112069-36-0; **9**, 112069-38-2; **12**, 106111-48-2; **13**, 97752-01-7; **14**, 106111-49-3; **15**, 97751-97-8; **16**, 69511-47-3; **17**, 5732-02-5; **18**, 23326-27-4; **19**, 112069-41-7; **20**, 112069-42-8; **21**, 112069-43-9; **22**, 112069-44-0; **23**, 112069-40-6; **24**, 112087-34-0; (*E*)-I, 112069-37-1; II, 109871-41-2; (*E*,*Z*)-PhCH=C(Ph)CH=$CHCH_2$N(Bu-*t*)COCH=$CH_2$, 39550-09-9; HC≡$CCH_2Br$, 106-96-7; $I(CH_2)_5I$, 628-77-3; $H_2C$=CHC(=$CH_2$)MgCl, 32657-89-9; $H_2C$=CHC(=C$H_2$)$(CH_2)_5I$, 112069-45-1; HC≡CLi, 1111-64-4; $H_2C$=CHC(=C$H_2$)$(CH_2)_5$C≡CH, 112069-46-2; *n*-$C_8H_{17}I$, 629-27-6; 2-*tert*-butyl-5,6-diphenyl-3a,6,7,7a-tetrahydrophthalimidine, 112069-39-3.

# Superacid-Catalyzed Electrophilic Formylation of Adamantane with Carbon Monoxide Competing with Koch-Haaf Carboxylation[1]

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**Abstract:** The superacid-catalyzed reaction of adamantane with carbon monoxide was investigated. 1-Adamantanecarboxaldehyde together with 1-adamantanecarboxylic acid and 1-adamantanol (the products of the reaction of intermediate 1-adamantyl cation) was obtained. The mechanism of the formation of 1-adamantanecarboxaldehyde by electrophilic formylation involving $\sigma$-insertion of the formyl cation is indicated. This is contrasted by the competing protolytic ionization of adamantane to 1-adamantyl cation which gives with CO 1-adamantanoyl cation and subsequently 1-adamantanecarboxylic acid (Koch-Haaf reaction) or by hydrolysis 1-adamantanol.

The reaction of alkyl or cycloalkyl cation with carbon monoxide giving acyl cations constitutes the key steps in the well-known Koch-Haaf reaction[2] used for the preparation of carboxylic acids from alkenes, CO, and water. Synthetic aspects of this reaction

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have been studied extensively and reviewed by Falbe.[3a] Kinetic and thermodynamic aspects of the various reaction steps have been investigated under stable ion conditions by Hogeveen.[3b] Generation of acyl cation by reaction of CO with the corresponding alkyl cations leads to the formation of a new carbon–carbon bond. Whether this process occurs by direct alkylation at carbon (eq 1) or alkylation at oxygen followed by an O → C alkyl shift (eq

$$R^+ + CO \rightleftharpoons R{-}C \equiv O^+ \quad (1)$$

$$R^+ + CO \rightleftharpoons R{-}O{-}C^+ \quad (2a)$$

$$R{-}O{-}C^+ \rightarrow R{-}C \equiv O^+ \quad (2b)$$

2) is still uncertain. While a similar intermediate as in eq 2a has been postulated[4] in the formation of carbenium ions from alkoxides and carbenes, theoretical justification for the mechanism was obtained from nonempirical calculations[5] on several configurations of a model system, e.g., protonated carbon monoxide.[6]

The parent of the acyl cations (R = H) is the formyl cation. In the course of acid-catalyzed formylation of aromatics with CO,[7,8] the formyl cation (protonated CO) is suggested to be the reactive electrophile. Electrophilic formylation of aromatics with CO in superacid media was explained by formylation by the protosolvated formyl cation.[7-11]

Whereas electrophilic formylation of aromatics with CO is well studied under both Gatterman–Koch condition and with superacid catalysis,[6-11] electrophilic formylation of saturated aliphatics remains virtually unrecognized. Electrophilic alkylation of saturated aliphatics with reactive alkyl cations was investigated by Olah and his co-workers.[12] The concept of three-center two-electron bond formation involving pentacoordinated carbonium ion transition states satisfactorily explains the mechanism of acid-catalyzed saturated hydrocarbon transformation reactions.[13] The scope of this concept has been extended to other electrophilic aliphatic reactions such as the nitration,[14a] halogenation,[14b] and oxygenation.[14c]

The formation of $C_6$ or $C_7$ acids along with some ketones was reported by Paatz and Weisberger in the reaction of isopentane, along with methylcyclopentane, and cyclohexane with CO in $HF:SbF_5$ at ambient temperatures and atmospheric pressure.[15a] Yoneda et al.[15b] have found that other alkanes can also be carboxylated with CO in $HF:SbF_5$. Tertiary alkyl cations which are produced by protolysis of C–H bonds of branched alkanes in $HF:SbF_5$ undergo skeletal isomerization and disproportionation before reacting with CO. Reactions of acyclic hydrocarbons of various skeletal structures with CO in superacid media were recently studied by Yoneda et al.[15c] Products obtained were only isomeric carboxylic acids with lower number of carbon atoms than the starting alkanes. Formation of the carboxylic acids were accounted by the reactions of parent, isomerized, and fragmented alkyl cations with CO to form the corresponding acyl cation intermediates (Koch–Haaf reaction) followed by their quenching with water. No formylated products have ever been identified in these reactions.

Recently Okamoto et al.[16a,2b] have obtained 3-hydroxy-4-homoadamantyl-1-adamantanecarboxylate by the triflic acid catalyzed reaction of 1-adamantyl triflate with carbon monoxide at atmospheric pressure and adamantane. They considered that the initial step involves the reaction of 1-adamantyl cation with CO giving the 1-adamantanoyl cation which then abstracts a hydride from adamantane giving 1-adamantanecarboxaldehyde. The transient aldehyde, however, never could be observed, which was suggested to be due to its fast further reaction under the reaction conditions. In patent literature[16c] a claim has been made for the preparation of 1-adamantanecarboxaldehyde by the $AlCl_3$-catalyzed reaction of adamantane with CO in $CH_2Cl_2$ at ≤ 25 °C. However, no details about the yield or mechanism of aldehyde formation were discussed.

Our continued interest in superacid-catalyzed reactions led us to investigate the reaction of CO wth adamantane (a model for saturated tertiary hydrocarbon) in some detail under mild reaction conditions.

## Results and Discussion

When adamantane is allowed to react with carbon monoxide under pressure (1200 psi) in trifluoromethanesulfonic (triflic) acid with an acid/adamantane molar ratio of 10:1 at room temperature in 1,1,2-trichlorotrifluoroethane (Freon-113) solution, 1-adamantanecarboxaldehyde was obtained in only 0.2% yield upon quenching the reaction mixture in ice–bicarbonate. 1-Adamantanecarboxylic acid, the usual Koch–Haaf product, is the major product. When the reaction is carried out in the much higher acidity superacid system $B(OSO_2CF_3)_3$–$CF_3SO_3H$ by using an acid/adamantane molar ratio of 3:1, the yield of 1-adamantanecarboxaldehyde increased to 3.4%. When the same reaction is repeated under identical reaction conditions and CO pressure in $SbF_5$–$CF_3SO_3H$ superacid system, the yield of 1-adamantanecarboxaldehyde was further improved to 8.2%. Just as the reaction in the $CF_3SO_3H$ system, reactions in higher acidity superacid systems also gave 1-adamantanecarboxylic acid as the major product (60–75%), together with an increased yield of 1-adamantanol (2–6%).

When all the superacid-catalyzed reactions of adamantane with CO were repeated under solvent-free condition by using only the excess of acid as the reaction medium, the yields of 1-adamantanecarboxaldehyde formed further increased (9.1, 14.5, and 21% in $CF_3SO_3H$, $B(OSO_2CF_3)_3$–$HSO_3CF_3$, and $SbF_5$–$HSO_3CF_3$ system, respectively).

Formation of 1-adamantanol and 1-adamantanecarboxylic acid in the reactions is indicative of initial protolytic ionization of adamantane to 1-adamantyl cation, according to Scheme I. In the superacid-catalyzed reactions of adamantane with olefins we

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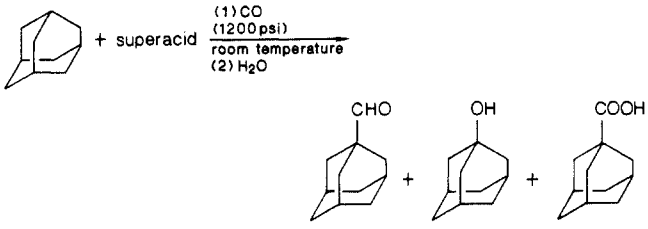
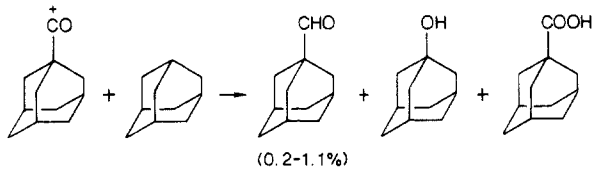



have previously discussed the adamantane–adamantyl cation equilibrium.[17a,17b] Adamantane remains in equilibrium with 1-adamantyl cation (or possibly with 1-adamantyl triflate in the case of triflic acid catalyzed reaction) in the conjugate superacids used. Quenching of the 1-adamantyl cation gives 1-adamantanol.

Kinetics of reversible carbonylation–decarbonylation as applied to acyclic and cyclic systems[18] were investigated by Hogeveen,[3] Olah,[19,20] Brouwer,[21] and others. It was found that both carbonylation and decarbonylation processes are very rapid. The off-planar *tert*-adamantyl cation was found to be 2.1 kcal less stable than tertiary acyclic cations, but the carbonylation equilibrium constant for the former system was found to be 30 times larger than those for acyclic systems.[3] The stabilization of positive charge in alkanoyl cations has been realized as mainly due to the resonance $RC^+{=}O \leftrightarrow RC{\equiv}O^+$. The effect of the R group on this stabilization is only of minor importance. Nevertheless, the magnitude of carbonylation–decarbonylation equilibrium constants provides a quantitative measure of the stabilization of the alkylcarboxonium ions in solution. In the superacid systems of the present investigation, 1-adamantanoyl cation formed from 1-adamantyl cation and CO remains in significant concentration under CO pressure and upon quenching provides 1-adamantanecarboxylic acid as the major product.

An alternative route by which 1-adamantanoyl cation or its protosolvated form can lead to 1-adamantanecarboxyaldehyde is by hydride abstraction from excess adamantane. The latter thus forms 1-adamantyl cation which reenters the reaction processes (Scheme I). To prove the feasible formation of 1-adamantanecarboxaldehyde by this route, 1-adamantanoyl cation was prepared from the reaction of 1-adamantanecarbonyl chloride with either $SbF_5$–$CF_3SO_3H$ or $SbF_5$.[19] Thus prepared adamantanoyl cation was then allowed to react with adamantane (serving as the hydride source) for comparable length of time as the reaction of adamantane with CO. Quenching the reaction mixture in ice–bicarbonate gave 0.2% and 1.1% 1-adamantanecarboxaldehyde, respectively, based on the formed 1-adamantanecarboxylic acid from 1-adamantanoyl cation in $SbF_5$–$CF_3SO_3H$ and $SbF_5$, respectively.




Formation of 1-adamantanecarboxaldehyde, albeit in low yield, shows that 1-adamantanoyl cation can abstract a hydride from adamantane. Hydride abstraction by alkanoyl cations to give aldehydes is seldom observed.

Brouwer[22] has reported the formation of acetaldehyde by hydride abstraction by the acetyl cation from isobutane. Olah et al. subsequently showed that in aprotic media the reaction does not take place.[23] In superacidic media protosolvation of the acetyl cation increases its reactivity allowing hydride abstraction from isobutane

$$CH_3CO^+\cdots HA + HC(CH_3)_3 \rightarrow CH_3CHO^+H + (CH_3)_3C^+$$

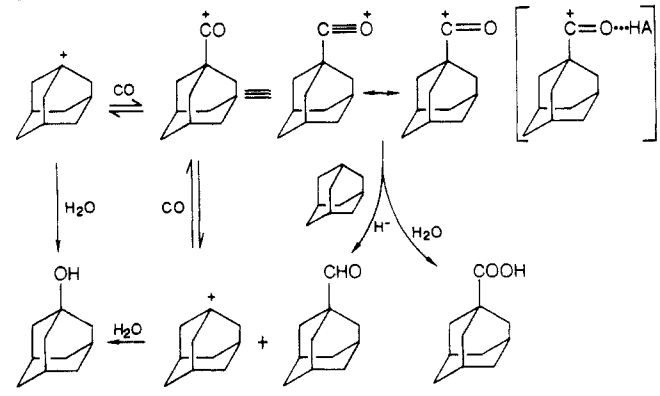
The yields of 1-adamantanecarboxaldehyde obtained via hydride abstraction by the adamantanoyl cation are much lower than those obtained in the reaction of adamantane with CO in the superacid media. It is, therefore, clear that hydride abstraction by 1-adamantanoyl cation generated from 1-adamantyl cation with CO in superacids is not the major route responsible for the formation of 1-adamantane carboxaldehyde in the former reaction.

To further study the validity of this conclusion we also investigated the reaction of 1,3,5,7-tetradeuterioadamantane with CO under comparable reaction conditions. 1,3,5,7-Tetradeuterioadamantane[24] was allowed to react with CO in the presence of $CF_3SO_3H$. Quenching of the reaction mixture with ice–bicarbonate and extraction in $CH_2Cl_2$ gave, along with the usual 1-adamantanol and 1-adamantanecarboxylic acid, 3,5,7-trideuterio-1-adamantanecarboxaldehyde-H and 3,5,7-trideuterio-1-adamantanecarboxaldehyde-D in 94:6 ratio (based on $^1H$ and $^2H$ NMR spectra with use of an internal standard).[25]

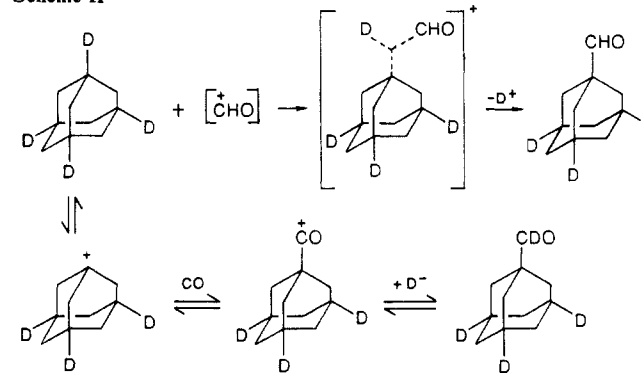
The above results conclusively show that the direct $\sigma$-insertion of formyl cation is the major pathway leading to the formation of 1-adamantanecarboxaldehyde (Scheme II). Intermolecular hydride (deuteride) abstraction by adamantanoyl cation appears to be only a minor reaction. In a control reaction of 1,3,5,7-tetradeuterioadamantane with triflic acid, no hydrogen–deuterium exchange was observed.

Both the formyl cation $HC^+O$ and isoformyl cation $CO^+H$ are known to exist in the gas phase.[25] Neither cation could so far be directly observed in solution under stable ion conditions. The

**Scheme I**




**Scheme II**

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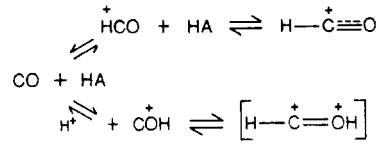
(24) 1,3,5,7-Tetradeuterioadamantane was prepared from the corresponding tetrabromoadamantane and $(n\text{-Bu})_3SnD$.

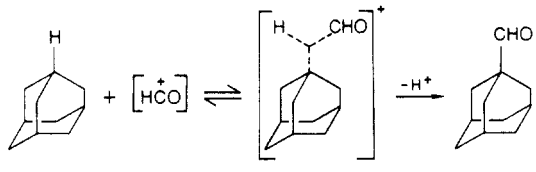
(25) The $CDCl_3$ and the proton impurities in it were used as internal standards.

reasonable solubility of CO in $CF_3SO_3H$ at atmospheric pressure[27] was used in an attempt to observe the elusive formyl cation. $^{13}C$-labeled CO was generated from $^{13}C$-labeled sodium formate in $SbF_5$–$CF_3SO_3H/SO_2ClF$ system under varying low-temperature conditions.[8] $^{13}C$ NMR showed only $^{13}CO$ but not the $H^{13}C^+O$ ion. In the course of present investigation, we attempted again to observe the elusive formyl cation by reacting $^{13}CO$ (99% enriched) with both $SbF_5$–$CF_3SO_3H$ and $B(OSO_2CF_3)_3$–$CF_3SO_3H$ at low temperature. Again the $H^{13}C^+O$ ion could not be observed by $^{13}C$ NMR.

Whereas the formyl cation could not be directly observed by NMR spectroscopy, its intermediacy has been well established in aromatic formylation reactions.[7-11] In order to account for the failure to observe the formyl cation we suggested that CO is protonated in acid media to generate protosolvated formyl cation,[7,8] a very reactive electrophile. Protosolvation of the carbonyl oxygen allows facile deprotonation of the methine proton, thus resulting in rapid exchange via involvement of the isoformyl cation.



In the present investigation, although the formyl cation still remained elusive and escaped spectroscopic detection, its intermediate formation is again indicated. The substantially higher yield of 1-adamantanecarboxaldehyde in the superacid-catalyzed reactions of adamantane with CO as compared with that obtained through the adamantanoyl cation can only be explained by direct formylation involving the insertion of the protosolvated reactive HCO ion into the C–H bond of adamantane ($\sigma$-formylation) at the bridgehead position. The transition state for this reaction is considered to be a three-center two-electron-bonded pentacoordinate carbocation which via proton elimination gives the aldehyde.



Balaban and Nenitzescu[28] in the aluminum trichloride catalyzed reaction of isobutane with CO reported the formation of methyl isopropyl ketone. Formation of pivalaldehyde from initial pivaloyl cation by hydride abstraction was suggested as an intermediate, which then rearranges to methyl isopropyl ketone. We repeated the reaction of isobutane with CO in superacid media with use of the $SbF_5$–$CF_3SO_3H$ system. The only product isolated is methyl isopropyl ketone. No pivalaldehyde could be detected. There is thus so far no evidence for direct insertion of the formyl cation into the C–H bond of isobutane.

The rigid cage framework of adamantane does not allow formation of any stable olefin and no back side (nucleophilic or electrophilic) attack is possible at the bridgehead positions. Furthermore, in the case of intermediate 1-adamantanoyl cation (generated from 1-adamantyl cation and CO) no intramolecular hydrogen or alkyl shifts are possible. As shown formation of 1-adamantanecarboxaldehyde via intermolecular hydride transfer is only a minor reaction. Direct electrophilic insertion of the formyl cation into the C–H bond of adamantane is, therefore, the major pathway leading to the formation of 1-adamantanecarboxaldehyde in superacid-catalyzed reactions of adamantane with CO. This reaction under the described reaction conditions competes effectively with the Koch–Haaf carboxylation reaction of adamantane.

The present work represents the first example of a superacid-catalyzed electrophilic formylation of a saturated hydrocarbon by CO competing with the Koch–Haaf carboxylation reaction.

## Experimental Section

Adamantane, 1-adamantanecarboxylic acid, 1-adamantanecarbonyl chloride, and 1-adamantanol were purchased from Aldrich. Triflic acid was distilled prior to use. 1,1,2-Trichlorotrifluoroethane (Freon-11o) was dried over phosphorus pentoxide through reflux. Boron triflate was prepared according to our previous procedure.[29] CO used (MG Scientific) was of highest purity.

Gas chromatographic analysis was carried out on a Varian Model 3700 gas chromatograph equipped with an on-line automatic integrator and a 30m fused silica capillary column (DB-1). GC–MS analysis was carried out on a Hewlett Packard mass spectrometer interfaced with a gas chromatograph. Infrared analysis was accomplished on a Perkin Elmer Model 1550 FTIR spectrometer. $^{13}C$ NMR spectra were recorded on a Varian VXR-200 instrument equipped with a variable temperature broad band probe.

From the reaction mixture of $SbF_5$–$CF_3SO_3H$ and $B(OSO_2CF_3)_3$–$CF_3SO_3H$, 1-adamantanecarboxaldehyde was isolated with use of an alumina column and hexane as eluent. The isolated aldehyde was characterized by FTIR (>C=O, 1730 $cm^{-1}$), $^1H$ and $^{13}C$ NMR spectroscopy.[30] $\delta$ $^1H$ 9.28 (CHO), $\delta$ $^{13}C$ $C_1$ 41.7, $C_2$ 38.5 (135.0), $C_3$ 27.3 (133.1), $C_4$ 36.5 (129.7), $C_a$ 205.5 (167.2).

From the reaction mixture of $CF_3SO_3H$, 1-adamantanecarboxaldehyde was identified by FTIR, GC–MS and confirmed by conjunction in the GC with a reference aldehyde: GC–MS *m/e* 164 (M, 6%), 136 (M – CHO + H, 12.1%), 135 (M – CHO, 100%), 107, 93, 81, 65.

**General Method of Reaction of Adamantane with CO.** A 100-mL stainless steel autoclave fitted with a Teflon liner was charged with adamantane (usually 2 g, 15 mmol) and 10-fold excess of triflic acid or threefold excess of either $B(OSO_2CF_3)_3$–$CF_3SO_3H$ (1:1) or $SbF_5$–$CF_3SO_3H$ (1:1) diluted in Freon-113 was added slowly with cooling under dry nitrogen. The autoclave was sealed, and CO (1200 psi) was then introduced. After 10 h at room temperature the autoclave was depressurized and opened, and the reaction mixture was quenched in ice–bicarbonate mixture. Products were twice extracted in $CH_2Cl_2$ and dried over anhydrous $Na_2SO_4$. A concentrated solution of reaction mixture was subjected to GC and GC–MS analysis.

**Reactions of 1-Adamantanecarbonyl Chloride with Superacids.** In a three-necked, dry flask connected to a dry nitrogen line a solution of $SbF_5$ (or $SbF_5$–$CF_3SO_3H$) in Freon-113 was cooled to 0 °C, and an equimolar amount of adamantanecarbonyl chloride in Freon-113 was added. The temperature was allowed to rise to room temperature, and the reaction was continued for 4–6 h after which it was worked up in the usual way as described above. 1-Adamantanecarboxaldehyde in these reaction mixtures was identified by FTIR and GC–MS and confirmed by coinjection with authentic aldehyde.

**Preparation of Authentic 1-Adamantanecarboxaldehyde.** In a dry, three-necked flask connected to a nitrogen line, 6 g (28 mmol) of pyridinium chlorochromate[31] was taken in 20 mL of dry $CH_2Cl_2$. To the well-stirred solution of pyridinium chlorochromate in $CH_2Cl_2$, a solution of 4.3 g (26 mmol) of 1-adamantanemethanol in 10 mL of $CH_2Cl_2$ was added in 1 portion. The reaction was monitored by GC to observe the disappearance of alcohol. After 20 min, the reaction was worked up by adding ether. By filtering the product solution and removing the ether, crude aldehyde was obtained 96% yield. The aldehyde was purified by an alumina column with use of hexane as eluent. 1-Adamantanecarboxaldehyde was characterized by FTIR and $^{13}C$ NMR spectroscopy.[30]

**Acknowledgment.** Support of our work by the National Institutes of Health is gratefully acknowledged.

**Registry No.** CO, 630-08-0; $F_3CSO_3H$, 1493-13-6; $B(OSO_2CF_3)_3$, 64371-01-3; $SbF_5$, 7783-70-2; $^+CHO$, 17030-74-9; *i*-PrMe, 75-28-5; AcPr-i, 563-80-4; adamantane, 281-23-2; 1-adamantanecarboxaldehyde, 2094-74-8; 1-adamantanol, 768-95-6; 1-adamantanecarboxylic acid, 828-51-3; 1,3,5,7-tetradeuterioadamantane, 19215-02-2; 3,5,7-trideuterio-1-adamantanecarboxaldehyde-*H*, 112196-18-6; 3,5,7-trideuterio-1-adamantanecarboxaldehyde-*D*, 112196-19-7; 1-adamantanemethanol, 770-71-8.

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